Structural and Spectroscopic Characterization of Dioxovanadium(V) Complexes with Asymmetric Schiff Base Ligands

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A wide range of asymmetric Schiff base ligands containing primary amine functions can be prepared in one step and in high yield by the reaction of $VO(OEt)_3$ with salicylaldehyde and the appropriate diamine. The resulting VO_2L complexes contain tridentate ligands with phenolate, imine, and amine coordination to the dioxovanadium(V) complex ion. An X-ray structure of one compound ([VO_2(1,2-pnSAL)], **5A**, where 1,2-pnSAL = 1(*N*-salicylideneamino)-2-aminopropane) demonstrates that it is a dimer in the solid state with a V_2O_4 core. However, when dissolved in DMSO, this material dissociates into monomers. Proton NMR spectroscopy reveals that the second isomer, **5B** [VO_2(1-amino-2(salicylideneamino)propane], is prepared in the process, but to a much lesser extent than **5A** (85:15). The reactivity of VO_2(enSAL) [enSAL = 1-(*N*-salicylideneamino)-2-aminoethane] with peroxides in neutral, basic, and acidic media is discussed. Significantly, the reported synthetic methodology does not yield successful VO_2(1-(*N*-salicylideneamino)-3-aminopropane) [VO_2(1,3-pnSAL)]. Instead, the V(IV) complex VO(SALPN)DMSO (**8**) is isolated and has been characterized structurally (SALPN = 1,3-bis-(*N*-salicylideneamino)propane). Although VO(SALPN)DMSO and VO(SALEN) have markedly different solution spectra, their reactivity with coordinating and noncoordinating acids are very similar. X-ray parameters: [VO_2(1,2-pnSAL)] (**5A**), $C_{10}H_{13}N_2O_3V$, 260.1 g/mol, triclinic crystal system, $P\bar{1}$, (No. 2), a = 7.270(2) Å, b = 7.686(2) Å, c = 11.082(4) Å, α = 72.16(2)°, β = 73.23(2)°, γ = 85.95(2)°, V = 564.2(3) Å^3, Z = 2, 2244 data collected with $5° < 2\theta < 50°$, 1786 data with $(F_o) \pm 0.6\sigma(F)$, R = 0.072, R_w = 0.097; [VO(SALPN)·DMSO] (**8**), $C_{19}H_{22}N_2O_4VS$, 425.4 g/mol, monoclinic crystal system, $P2_1$, (No. 14), a = 11.436(3) Å, b = 7.775(2) Å, c = 11.661(2) Å, β = 109.47(2)°, V = 977.5(3) Å^3, Z = 2, 6224 data collected in the range $5° < 2\theta < 55°$, with 4240 data with $(F_o) \pm 0.6\sigma(F)$, R = 0.054, R_w = 0.062.

Introduction

The chemistry of vanadium in the biosphere has received increased attention in recent years.[4] While the vanadium requirement for mammals is at the nano- to picomolar level, several lower organisms have a requirement for this element which is considerably more pronounced.[5] Ascidians accumulate vanadium at levels up to 10^7-fold over their marine environment,[6] and the mushroom *Amanita muscaria* accumulates vanadium to produce the natural product amavadin.[7] Two enzymes have been isolated with a unique requirement for vanadium: (1) an alternative nitrogenase from several species of *Azotobacter*[8] and (2) a haloperoxidase from many marine algae.[9,10] While the catalytic function is known for the two enzymes, the mechanism of catalysis is ill-defined for these systems.

Vanadium haloperoxidases catalyze the reaction shown in eq 1. X-ray absorption,[11] electron paramagnetic resonance,[12] electronic and ^{51}V-NMR spectroscopies[13a,b] have been used to probe

$$RH + H^+ + X^- + H_2O_2 \rightarrow RX + 2H_2O \qquad (X = Cl^-, Br^-, I^-) \quad (1)$$

the structure of the metal center. The structure that is emerging for the active site contains a mononuclear vanadium(V) that is likely found as either a monooxovanadium(V) (VO^{3+}) or a vanadate ester ($VO(OR)^{2+}$). It is unlikely that tyrosine is bound to a VO^{3+} core since strong phenolate to metal charge transfer excitations not found in the enzyme are associated with this structural type.[14] Imidazole coordination to vanadium(V) has been inferred[15] based on ESEEM measurements of the reduced, catalytically inactive enzyme. The identity of the ligands and the number of individual O and N donor atoms bound is not

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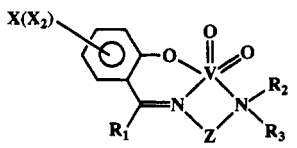

	Complex No.	$X(X_2)$	R_1	Z in the Diamine	R_2	R_3
Aldehydes						
	1	H	H	$-CH_2-CH_2-$	H	H
	2	5-Br	H	$-CH_2-CH_2-$	H	H
	3	3,5-Cl_2	H	$-CH_2-CH_2-$	H	H
	4	3-OMe	H	$-CH_2-CH_2-$	H	H
	5A	H	H	$-CH(Me)-CH_2-$	H	H
Ketones						
	6	H	Me	$-CH_2-CH_2-$	H	H
	7	H	Ph	$-CH_2-CH_2-$	H	H

Figure 1. Ligands used in this study.

known with certainty, but it is thought that the first coordination sphere includes at least four O atoms and up to two N atoms.[11,15]

As part of our continuing interest in elucidating the coordination environment surrounding the vanadium atom in the enzyme, vanadium bromoperoxidase (VBrPO), and in defining the catalytic mechanism of this enzyme, we have synthesized a novel class of vanadium(V) complexes of the generic type VO_2L, in which L is an unusual tridentate ligand. The ligands, illustrated in Figure 1, are mono(Schiff bases) formed from the condensation of only 1 equiv of salicylaldehyde (or a 2-hydroxyaromatic ketone) with ethylenediamine or 1,2-diaminopropane. This *in situ* ligand synthesis–complex formation stands in sharp contrast to the usual bis(Schiff base) complex formation known to occur for V(IV) complexes (e.g. VO(SALPN)[16] and VO(SALEN)).[17] The only other reported synthesis of such primary amine complexes involves other metal ions, and the yields and synthetic simplicity are not as rewarding.[18,19] We present in this paper the details of the synthesis and unequivocal characterization of this interesting and novel class of VO_2L complexes by means of spectroscopic data (NMR, MS, UV–vis, and IR) and a single crystal X-ray structure (for one of the analogs) that corroborates the spectroscopic structural assignments.

Experimental Section

Materials. Absolute EtOH was purchased from Midwest Grain Products Co., and absolute MeOH was obtained from J. T. Baker Co. All other solvents (ChromAR HPLC grade) were obtained from Mallinckrodt Chemical Co. Both 3,5-dichlorosalicylaldehyde, [HSALCl$_2$], and 5-bromosalicylaldehyde, [HSALBr], were obtained from Pfaltz and Bauer Chemical Co. and used as received. All other reagents were purchased from Aldrich Chemical Co. and also used as received.

Abbreviations Used: en = ethylenediamine; pn = 1,2-diaminopropane; dmphen = 4,5-dimethyl-1,2-phenylenediamine; HSAL = salicylaldehyde; HSALBr = 5-bromosalicylaldehyde; HSALCl$_2$ = 3,5-dichlorosalicylaldehyde; HSALOMe = 3-methoxysalicylaldehyde; HenSAL = 1-(*N*-salicylideneamino)-2-aminoethane; HenSALBr = *N*-(5-bromosalicylideneamino)-2-aminoethane; HenSALCl$_2$ = *N*-(3,5-dichlorosalicylideneamino)-2-aminoethane; HenSALOMe = *N*-(3-methoxysalicylideneamino)-2-aminoethane; HpnSAL = (*N*-salicylideneamino)-2-aminopropane isomers (1- and 2-substituted)]; HenHOAcetPh = *N*-(1-(2-hydroxyphenyl)phenylmethylidene)-ethylenediamine; HenHOBzPh = N-((2-hydroxyphenyl)methylmethylidene)ethylenediamine; H_2SALEN = *N*,*N*′-bis(2-salicylideneamino)-ethane; H_2SALPN = 1,3-bis(*N*-salicylideneamino)propane; H_2SHED = *N*-(salicylideneamino)-*N*′-(2-hydroxyethyl)ethylenediamine; H_2SALAHE = 1-(salicylideneamino)-2-hydroxyethane.

Triethyl Vanadate. The triethyl ester of vanadic acid, VO(OEt)$_3$, was prepared *in situ* via a modified literature procedure.[20] In a typical preparation, finely ground V_2O_5(s) was refluxed in absolute EtOH overnight. The resultant olive green-colored slurry was cooled to room temperature and then filtered through a tared fritted glass filter to yield a clear, colorless-to-pale yellow solution of VO(OEt)$_3$. The filtered solid was dried under nitrogen, and the mass was determined. Typically, the mass of this solid was approximately 15% of the starting mass of V_2O_5(s). The yield of VO(OEt)$_3$ was calculated from the difference in the starting and recovered masses of V_2O_5(s), assuming that the recovered solid was unreacted V_2O_5(s). [*Caution!* Use care in handling this reagent since it is moderately volatile (although less volatile than the analogous trimethyl ester, VO(OMe)$_3$) even as a dilute solution in EtOH.]

Generic Synthesis of VO_2L Complexes. The following procedure is the preferred method of synthesis of VO_2L complexes. The scale of reaction can vary widely in VO(OEt)$_3$ (1.3–20 mmol were used). Reagents are added in the following order: VO(OEt)$_3$; diamine; aldehyde (or ketone). Typically, a diamine (10.0 mmol) in 5–10 mL of absolute EtOH was added to the clear solution of VO(OEt)$_3$ (10.0 mmol) in 250 mL of absolute EtOH, which produced immediately an intractable off-white intermediate of unknown identity. To the slurry of this intermediate was added dropwise the desired salicylaldehyde or 2-hydroxyaryl ketone (10.0 mmol) in 10–20 mL of absolute EtOH. The yellow-colored VO_2L complexes formed quickly upon addition of the aldehyde, but more slowly with the ketones. After refluxing and/or stirring of this slurry for 2 h (for aldehydes) to 12 h (for ketones), the reaction mixture was filtered, and the isolated solids were washed twice with cold absolute EtOH followed by Et_2O and then dried in air via suction. Typical yields of unrecrystallized VO_2L complexes ranged from 85% to 99%. VO_2L complexes were purified by recrystallization either from a saturated solution of DMSO at 70 °C or by addition (at room temperature) of an equal volume of either MeOH or H_2O to a concentrated solution of VO_2L in DMSO followed by refrigeration (0 °C). Detailed syntheses for **5** and **8** are presented below while procedures for **1-4**, **6**, and **7** are given in the supplementary material.

[1-*N*-(salicylideneamino)-2-aminopropanato](dioxo)vanadium(V) Isomers, A and B, VO_2(1,2-pnSAL) (5). Employing the generic synthesis procedure above, 1,2-pn (1.28 g; 17.3 mmol) and HSAL (2.11 g; 17.3 mmol) were added to VO(OEt)$_3$ (17.3 mmol) in preparing crude **5** (4.35 g; 89% yield). Using the DMSO/MeOH pair of solvents as mentioned above, a pure crystalline product was obtained (76% recovery). The product was recrystallized further (2×) to obtain single crystals that were suitable for X-ray structural analysis. Anal. Calcd for $C_{10}H_{13}N_2O_3V$ (MW = 260.17): C, 46.17; H, 5.04; N, 10.77. Found: C, 46.28; H, 5.16; N, 11.11. ^{1}H-NMR in DMSO-d_6, (δ (ppm), multiplicity, integration); isomer A, 8.87, s, 0.84 H; 3.80 (A_2B_2), m, 3.4 H; 1.15, d, 2.5 H; 5.16 br, m, <2H;[21] isomer B, 8.89, s, 0.164 H; 1.30, d, 0.5 H ; (A_2B_2) 2.67 & 2.81, m, 0.6 H; 5.20 br, s, <0.3H. ^{51}V NMR (5 mM in DMSO-d_6 solution) (δ(V) (ppm), multiplicity): −553, s. MS(FAB)$^+$: 261 (M + 1); MS(FAB)$^-$: 259 (M − 1); UV–vis spectral data in DMSO [nm (ϵ, M^{-1} cm^{-1})]: 370 (3.2×10^3), 259 (1.2×10^4). Important IR frequencies (using KBr disks) in cm^{-1}: 3472, 3238, 3215, 3122.

[*N*,*N*′-Bis-(salicylideneamino)ethanato](oxo)vanadium(IV)–Dimethyl Sulfoxide, VO(SALpn)DMSO (8). Intending to carry out the generic synthesis procedure above, we slowly added 1,3-diaminopropane (1.19 g; 16.0 mmol) in EtOH to an ethanolic solution of VO(OEt)$_3$ (16.0 mmol), leading to the formation of the usual off-white-to-yellow intermediate. Subsequent addition of HSAL (2.52 g; 16.0 mmol) in 10 mL of EtOH to the reaction mixture followed by heating to reflux produced a burgundy-colored solution. This solution was refluxed overnight, and then cooled to ambient temperature. The resultant orange product was filtered, washed with cold absolute EtOH, and then dried in air via suction to obtain crude product (1.84 g; 44% yield). The color of the filtrate was a deep burgundy. A pure microcrystaline solid was obtained (76% recovery) using the DMSO/H_2O solvent system. Crystals suitable for single-crystal X-ray structural analysis of **8** were obtained (at ambient temperature) by allowing H_2O vapor to slowly diffuse into a saturated solution of purified **8** in DMSO. Anal. Calcd for $C_{19}H_{22}N_2O_4SV$ (MW

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(21) These protons integrate to values less than two because they are in exchange with D$^+$ from a small amount of D_2O in solution.

Table I. Condensed Crystallographic Data for $[VO_2(1,2\text{-pnSAL})]$ (**5A**), and [VO(SALpn)·DMSO] (**8**)

	$[VO_2(1,2\text{-pnSAL})]$ (**5A**)	[VO(SALpn)·DMSO] (**8**)
formula	$C_{10}H_{13}N_2O_3V$	$C_{17}H_{16}N_2O_3V$·DMSO
mol wt	260.168	425.40
a, Å	7.270(2)	11.436(3)
b, Å	7.686(2)	7.775(2)
c, Å	11.082(4)	11.661(2)
α, deg	72.16(2)	90.000
β, deg	73.23(2)	109.47(2)
γ, deg	85.95(2)	90.000
V, Å^3	564.2(3)	977.5(3)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
Z	2	2
radiation	Mo Kα (0.7107 Å)	Mo Kα (0.7107 Å)
temp	ambient	ambient
no. of unique data	1980	4484
no. of obsd data	2240	6224
R^a	0.0721	0.0538
$R_w{}^b$	0.0973	0.0617

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

= 425.34): C, 58.80; H, 4.64; N, 8.07. Found: C, 58.56; H, 4.44; N, 8.08. MS(FAB)$^+$: 426 (M + 1); UV–vis spectral data in DMSO [nm (ϵ, M^{-1} cm^{-1})]: 762 (82), 508 (167).

Physical Measurements. X-ray Crystallography. Single crystals of **5A** and **8** were acquired as described above and mounted in sealed glass capillaries. A small amount of mother liquor was included in the capillary of **8** to decrease decomposition due to solvent loss from the crystal lattice. Diffraction data were collected on a Siemens R3m/v diffractometer at ambient temperature. Intensity data were obtained by using Mo Kα radiation (0.7107 Å) monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. Three standard reflections were measured every 97 reflections. For both compounds, random fluctuations of less than 3% were observed for three standard reflections. Lattice parameters were determined from a least squares refinement of 25 reflection settings for **8** and 30 reflection settings for **5A** obtained from an automatic centering routine. Table I contains a summary of data collection conditions and results for each structure. The data were reduced and the structure was solved by direct methods using the program SHELXTL PLUS[22] mounted on a VAX Station 3500. In subsequent refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The agreement indices $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were used to evaluate the results. Atomic scattering factors are from ref 23. Hydrogen atoms were included using a riding model (d_{C-H} = 0.96 Å, isotropic U(H) fixed at 1.20 U(eq) for **5A**), and the hydrogen atoms for **8** were allowed to refine isotropically. Structure determination summaries are outlined in Table I. Fractional atomic coordinates for **5A** and **8** are provided in Tables II and III, respectively.

The structure of **5A** showed evidence of disorder for two carbons of the propylene diamine ligand. The disorder has been modeled as two slightly different orientations for C9 and C10 at refined occupancies of 0.63(1) and 0.37(1) for the two configurations, respectively. No attempt was made to place the disordered partial hydrogen of C9. For clarity, the ORTEP plot shown as Figure 2 contains only the principally occupied orientation. Coordinates for both orientations are retained in the tables.

In **8** the DMSO molecule is disordered with the sulfur atom occupying alternate sites at refined occupancies of 0.63 and 0.37. Only one site is shown in the ORTEP drawing (Figure 3) for clarity. The disorder is essentially a consequence of an inversion of the pyramidal configuration of the sulfur. The carbons of the DMSO are placed at full occupancy. The hydrogens of the DMSO molecule were placed in calculated positions, d(C–H) = 0.96 Å with fixed U(H) ≈ 1.2U(eq) of the attached carbon atom.

Mass Spectrometry. Positive and negative FAB mass spectra were acquired by the University of Michigan Mass Spectroscopy facility. All VO_2L-type complexes were examined using (1) fast atom bombardment mass spectrometry employing positive [MS(FAB)$^+$] and negative [MS(FAB)$^-$] ion detection and (2) by electron impact (EI) mass spectrometry on a solid probe. All complexes studied by MS(FAB)$^+$ and MS(FAB)$^-$ showed mass peaks (however weak in intensity) corresponding to (M + 1) and (M – 1) mass species, respectively, and two complexes (**1** and **5**) exhibited base peaks corresponding to their molecular ions. The MS(FAB)$^+$ and MS(FAB)$^-$ spectra are consistent with the formulation of these complexes as VO_2L complexes. For complex **8**, only a MS(FAB)$^+$ was obtained. Mass peaks considerably greater than M observed in the MS(FAB)$^+$ of all VO_2L complexes provide evidence for the presence of dimeric and, in some instances, trimeric forms of VO_2L in addition to the monomeric forms.

The base peaks for all complexes examined by EI mass spectrometry (except for **3**) corresponded to oxovanadium (IV) complexes incorporating the tetradentate ligand which would be formed by condensing 2 equiv of the salicylaldehyde (or 2-hydroxy ketone) with the appropriate diamine. For example, the EI mass spectrum of **1** is dominated by the molecular ion peak which corresponds to the well-known complex VO(SALEN).

^{51}V NMR and ^{1}H NMR Spectroscopies. The ^{51}V NMR spectra of seven diamagnetic VO_2L complexes were recorded using ~5 × 10^{-3} M

Table II. Fractional Atomic Coordinates of the Non-Hydrogen Atoms of $[VO_2(1,2\text{-pnSAL})]$ (**5A**)

atom	x	y	z	U_{eq},^{a} Å^2
V1	0.0935(1)	0.3544(1)	0.42254(8)	0.0407(4)
O1	0.2141(5)	0.5524(4)	0.2715(3)	0.048(1)
O2	–0.1264(5)	0.4381(5)	0.4577(3)	0.048(1)
O3	0.0855(7)	0.1938(5)	0.3578(4)	0.065(2)
N1	0.3795(7)	0.3074(6)	0.4463(4)	0.051(2)
N2	0.0447(8)	0.1762(6)	0.6178(5)	0.052(2)
C1	0.3907(8)	0.5792(6)	0.1916(5)	0.047(2)
C2	0.421(1)	0.7058(8)	0.0663(6)	0.064(3)
C3	0.606(1)	0.739(1)	–0.0195(7)	0.083(3)
C4	0.761(1)	0.652(1)	0.0133(8)	0.088(4)
C5	0.7365(9)	0.530(1)	0.1372(7)	0.071(3)
C6	0.5502(8)	0.4891(7)	0.2291(5)	0.051(2)
C7	0.5344(8)	0.3677(7)	0.3578(6)	0.052(2)
C8	0.388(1)	0.195(1)	0.5797(6)	0.075(3)
C9A	0.227(1)	0.076(1)	0.6420(9)	0.057(4)
C9B	0.193(2)	0.178(2)	0.681(1)	0.056(6)
C10A	0.209(3)	–0.004(3)	0.787(2)	0.074(7)
C10B	0.174(7)	0.038(6)	0.821(4)	0.11(2)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_i a_j$.

Table III. Fractional Atomic Coordinates of the Non-Hydrogen Atoms of [VO(Salpn)·DMSO] (**8**)

atom	x	y	z	U_{eq},^{a} Å^2
V1	0.77021(5)	0.00000	0.16326(4)	0.0333(2)
O1	0.7069(2)	–0.1639(4)	0.2025(2)	0.0464(9)
O2	0.7750(2)	–0.0717(4)	0.0033(2)	0.0436(8)
O3	0.9477(2)	–0.0519(3)	0.2295(2)	0.0401(8)
N1	0.5998(3)	0.1212(4)	0.0726(3)	0.041(1)
N2	0.7886(3)	0.1276(4)	0.3277(3)	0.040(1)
C1	0.7188(3)	–0.0056(6)	–0.1050(3)	0.0372(9)
C2	0.7551(4)	–0.0603(6)	–0.2040(4)	0.047(1)
C3	0.6988(4)	0.0107(8)	–0.3188(4)	0.055(1)
C4	0.6057(4)	0.1295(7)	–0.3416(4)	0.054(2)
C5	0.5651(4)	0.1786(6)	–0.2478(3)	0.048(1)
C6	0.6200(3)	0.1135(5)	–0.1291(3)	0.039(1)
C7	0.5615(4)	0.1599(5)	–0.0410(3)	0.043(1)
C8	0.5157(4)	0.1652(7)	0.1406(4)	0.051(1)
C9	0.5802(5)	0.2683(7)	0.2553(4)	0.055(2)
C10	0.6750(4)	0.1670(7)	0.3550(4)	0.051(1)
C11	0.8921(4)	0.1690(5)	0.4098(3)	0.043(1)
C12	1.0141(4)	0.1282(5)	0.4081(3)	0.041(1)
C13	1.1163(4)	0.1942(6)	0.5039(4)	0.052(1)
C14	1.2346(4)	0.1537(7)	0.5151(4)	0.063(2)
C15	1.2567(4)	0.0444(6)	0.4310(4)	0.057(2)
C16	1.1604(3)	–0.0243(6)	0.3363(3)	0.047(1)
C17	1.0368(3)	0.0164(5)	0.3209(3)	0.036(1)
S1A	0.8191(2)	0.4296(2)	0.1045(2)	0.0513(6)
S1B	0.9259(2)	0.3537(4)	0.1220(3)	0.0465(9)
O4	0.8400(4)	0.2498(4)	0.1177(3)	0.076(2)
C18	0.9336(6)	0.5334(6)	0.2234(6)	0.086(3)
C19	0.8767(9)	0.493(1)	–0.0135(6)	0.142(4)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_i a_j$.

(22) SHELXTL PLUS. Siemens Analytical Instruments, Inc. Madison, WI, 1988.
(23) Ibers, J.; Hamilton, W., Eds. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974, Vo. IV, Tables 2.2 and 2.3.1.

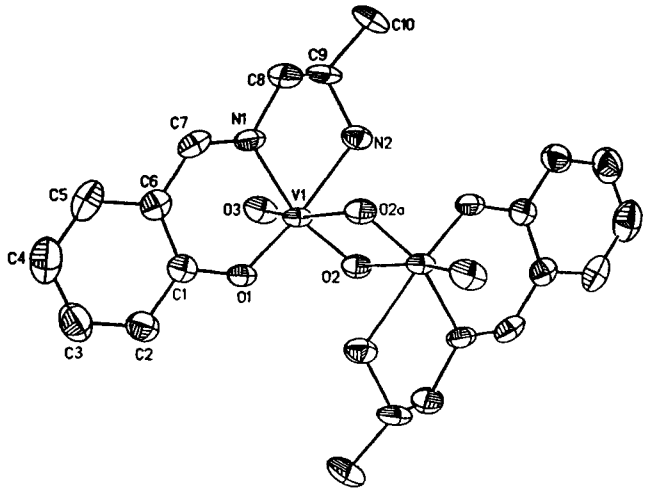


Figure 2. ORTEP diagram of $[VO_2(1,2\text{-pnSAL})]_2$ with thermal ellipsoids at 50% probability. Only the predominant isomer for the disordered pn chelate is shown.

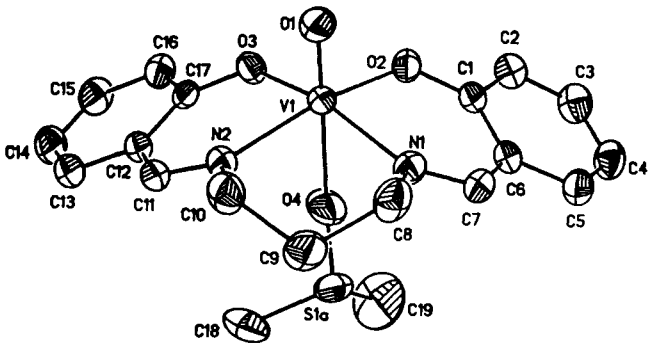


Figure 3. ORTEP diagram of VO(SALPN)DMSO (**8**) with thermal ellipsoids at 50% probability. Only the predominant conformation for the disordered DMSO is shown.

solutions in DMSO. The ^{51}V NMR spectra were collected using a Bruker AM200 instrument at 52.62 MHz utilizing 8K or 16K data points over a 125 000 Hz spectral window. Chemical shifts are reported in ppm versus external $V^V(O)Cl_3$ (0 ppm). Typically, 1000–10 000 transients were acquired using a 90° pulse (14 μs) and no prepulse delay. The free induction decay was appodized via exponential multiplication which induced 10 Hz of line broadening. A single broad transition was observed for each complex and chemical shifts were essentially invariant, ranging from −553 to −556 ppm. Proton NMR spectra were collected on a Bruker WM 360 spectrometer operating at 360.13 MHz. The ^1H data were collected on ~ 3 mM samples in DMSO-d_6, and the chemical shift was referenced to TMS via the residual solvent protons which were assigned the value of 2.49 ppm.

Other Measurements. UV–vis spectra were recorded on a Perkin Elmer Lambda 9 instrument. FTIR spectra were recorded by means of a Nicolet 5DX instrument on KBr pellets. Elemental analyses were performed either by Galbraith Laboratories, Knoxville, TN, or the Microanalysis Laboratory in the Department of Chemistry at the University of Michigan. Vapor pressure osmometry was performed by Galbraith Laboratories using DMF maintained at 70 °C. Vapor pressure readings for three solution concentrations were plotted to obtain a zero concentration vapor pressure from which a molecular weight was calculated.

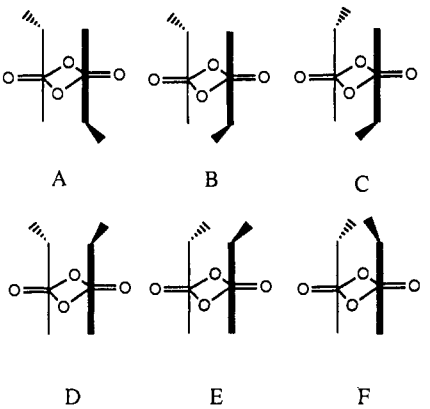
Results

Description of Structures. $[VO_2(1,2\text{-pnSal})]_2$. An ORTEP diagram of **5A** is illustrated in Figure 2, and important bond lengths and angles are provided in Table IV. The structure demonstrates that each V(V) ion is six coordinate with two distinct oxo groups being apparent. The V1–O3 bond has a typical V=O distance of 1.619 Å. The second oxo group is involved in the bridge between V1 and V1′. It is strongly coordinated to V1 (V1–O2, 1.665 Å) and is weakly associated with V1′ (V1′–O2, 2.427 Å). The remaining three coordination sites are occupied by the phenolate oxygen (V1–O1, 1.915 Å), imine nitrogen (V1–N1, 2.162 Å) and primary amine nitrogen (V1–N2, 2.120 Å) atoms of the ligand. Thus, the coordination spheres of the vanadium ions are composed of six unique heteroatom types: vanadyl oxo, two bridging oxo atoms at short and long distances, phenolate oxygen, and imine and amine nitrogen atoms. The polyhedron that is described resembles two edge shared octahedra that are significantly distorted. The O2–V1–O3 angle is 107.5°, a value that is close to that observed for VO_2EDTA,[24] $VO_2(8\text{-quinolate})_2$,[25] $[VO_2(HSHED)]_2$,[26] and many other *cis*-VO_2^+ (pervanadyl) units. Angles described by *trans* substituents are far from 180° ranging from 152.7 to 171.5°. The two $VO_2(1,2\text{-pnSal})$ units are related by an inversion center with a vanadium–vanadium distance of 3.222 Å.

Table IV. Important Bond Lengths (Å) and Angles (deg) for $[VO_2(1,2\text{-pnSAL})]$ (**5A**)

V1–O1	1.915(4)	O1–V1–O2	98.8(2)
V1–O2	1.665(4)	O1–V1–O2A	83.1(2)
V1–O2A	2.427(5)	O1–V1–O3	102.4(3)
V1–O3	1.619(6)	O1–V1–N1	84.4(2)
V1–N1	2.162(5)	O1–V1–N2	156.1(2)
V1–N2	2.120(7)		
O2–V1–O2A	77.7(2)	O2A–V1–N2	78.2(2)
O2–V1–O3	107.5(2)	O3–V1–N1	98.2(2)
O2–V1–N1	152.7(3)	O3–V1–N2	94.7(3)
O2–V1–N2	91.7(2)	N1–V1–N2	76.7(2)
O2A–V1–O3	171.5(2)	V1–O2–V1A	102.3(2)
O2A–V1–N1	75.7(2)		

Chart I



A single Schiff base condensation onto an asymmetric diamine such as 1,2-pnSAL will lead to two distinct isomers with the imine nitrogen either α or β to the chiral carbon atom. The ORTEP diagram in Figure 2 demonstrates that a crystal of the complex containing the β-imine linkage was structurally characterized. However, as we describe below, solution studies indicate that both isomer types result from this synthetic approach.

As shown in Chart I, additional isomers are possible once the ligand is bound to vanadium and a dimeric structure is adopted. Three sets of isomers may form an antiparallel orientation with phenolate moieties arranged on opposite sides of the V_2O_2 cores (A–C). Three other sets (D–F) have a parallel orientation. Each of the three sets within a parallel/antiparallel group are distinguished by the methyl group positions which have *syn* or *anti* conformations. The methyl groups are *syn* when located on the same ligand face as the terminal oxo group that is perpendicular to the 1,2-pnSAL plane and *anti* when located on the opposite face. The A and D isomers result when both methyls are in *syn* positions while C and F result from *anti* configurations. Mixed *syn*/*anti* isomers lead to structures B and E. As shown in Figure 2, the antiparallel, *anti*–*anti* isomer, C, is the structurally characterized form.

(24) Wieghardt, K.; Hahn, M.; Swirdoff, W.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 491.
(25) Scheidt, W. R.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3878.
(26) Li, X.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1988**, *27*, 4657.

Table V. Important Bond Lengths (Å) and Angles (deg) for [VO(SALpn)·DMSO] (**8**)

V1–O1	1.605(3)	V1–N1	2.105(3)
V1–O2	1.965(2)	V1–N2	2.107(2)
V1–O3	1.958(2)	V1–O4	2.230(3)
V1–O4–S1A	145.5(2)	O1–V1–N1	93.9(1)
V1–O4–S1B	152.3(3)	O1–V1–N2	91.8(1)
O1–V1–O12	101.7(1)	O1–V1–O4	172.0(1)
O1–V1–O3	103.3(1)		
O2–V1–O3	87.89(9)	O3–V1–N2	87.8(1)
O2–V1–N1	88.0(1)	O3–V1–O4	82.4(1)
O2–V1–N2	166.4(1)	N1–V1–N2	92.4(1)
O2–V1–O4	84.0(1)	N1–V1–O4	80.5(1)
O3–V1–N1	162.7(1)		

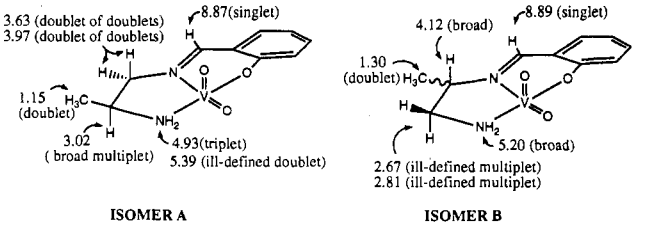
Comparison of 5a to Related Vanadium Complexes. Although a common structural motif in fused polyvanadates, the V_2O_4 core is rarely observed in discrete coordination compounds. We have reported two forms of $[VO_2(HSHED)]_2$ that have very similar coordination environments.[26] The most significant difference between HSHED and pnSal is that the former has a coordinated secondary amine while the latter has a bound primary amine nitrogen. This leads to a significant elongation of V–N bond from 2.120 to 2.202 Å in $[VO_2(HSHED)]_2$. Wieghardt has reported[27] the structure of $V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2Br_2$, a bis($\mu$-hydroxy)-bridged vanadium(IV) dimer, and we prepared[28] $[VO(SALAHE)]_2$, a bis(μ-alkoxy)-bridged V(IV) dimer. The core of the first molecule is similar to that reported herein for the bis(μ-oxo)-bridged vanadium(V) dimer, $[VO_2(1,2\text{-}pnSal)]_2$. The V(IV)–V(IV) distance is 3.033 Å as compared to 3.222 Å for **5A**. One expects the acute O2–V1–O2A angle (77.7°) and the obtuse V1–O2–V1A angle (102.3°) since metal–metal bonding is not possible in **5A**. This is also observed for the $[9]aneN_3$ complex, which is weakly antiferromagnetically coupled, but is unlike the metal–metal singly bonded, d_1–d_1 $Mo_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2$, which has an obtuse O1–Mo1–O1′ angle and an acute Mo1–O1–Mo1′ angle.[29] As was the case with $[VO_2(HSHED)]_2$, asymmetric μ-oxo bridges are seen for **5A**. This illustrates that the V1–O2 bond (1.665 Å) is essentially V=O (as compared with V1–O3 at 1.619 Å), whereas V1–O2A is much longer (2.427 Å).

Description of the Structure of VO(SALPN)DMSO. The structure of V(IV)O(SALPN)·DMSO (Figure 3) is similar to that described in a previous report[16] in which the compound crystallized as a linear, oxo-bridged, infinite chain. Important bond lengths and angles are provided in Table V. In the present structure the molecule forms discrete units with a DMSO oxygen atom in the sixth coordination site. The vanadium atom is 0.270 Å above the best N_2O_2 least-squares plane of SALPN with a long distance, 2.230(3) Å, to the DMSO oxygen. There are three examples of discrete, mononuclear VO(SAL(EN or PN)) complexes that can be compared. The trend in V=O bond length is $V^{V}O(SALEN)ClO_4$[13b,c] (1.576 Å) < $V^{IV}O(SALEN)$[17] (1.588 Å) < $V^{IV}O(SALPN)$ (1.605 Å). One does not observe a sixth ligand in the $V^{IV}O(SALEN)$ structure while aquo and perchlorate molecules bind to $[VO(SAL\text{-}EN)]^+$ and terminal oxo or DMSO are coordinated to $V^{V}O(SALPN)$. This may explain why $V^{IV}O(SALPN)$·DMSO and $[VO(SALPN)]_n$ are orange and $V^{IV}O(SALEN)$ is blue-green.

Discussion

Synthesis. A series of structurally novel VO_2L complexes has been prepared both in high yield and in high purity. While tridentate Schiff base complexes containing an exposed primary amine have been prepared[18,19] with other transition metals, the overall yields and synthetic simplicity of the reactions do not approach those of the VO_2L syntheses. The general method of synthesis involves addition of the diamine to an ethanol solution of $VO(OEt)_3$, followed by addition of the appropriate aldehyde or ketone. The series of reported complexes with variations in the aldehyde/ketone and diamine proportions of the ligand resulted from an attempt to find a derivative complex with higher solubility. The majority of the analogs originate from variations in the nature of the diamine and the type of aldehyde. Additionally, two analogs have been prepared by incorporating ketones into the system. The VO_2L complexes having terminal primary amine groups (**1–7**; Figure 1) are part of a more extensive series of compounds in which the terminal amines are also secondary and tertiary.[30]

Chart II



ISOMER A ISOMER B

The nature and course of the synthesis and yields of VO_2L products are affected by several parameters which include (1) the order of reagent addition and (2) the nature of the starting reagents (i.e., type of vanadium salt, diamine, hydroxy-substituted aldehyde, or ketone), solubility of the final product, and difference in the intrinsic reaction rates for aldehydes versus ketones. The synthesis of **1** was studied extensively and provided insight into the overall reaction systematics. Optimal yields are obtained by adding reagents in the order $VO(OEt)_3$, diamine, and then aldehyde or ketone. While variation in the optimal order does not preclude the synthesis of the desired VO_2L complex, it can lead to a substantial reduction in yields and purity, including an increased proportion of side reactions. The latter is likely the result of redox processes producing V(IV) species which, in turn, can be reoxidized by atmospheric oxygen to V(V) in producing the desired complex.

Quite surprisingly, a seemingly subtle change in the nature of the diamine used (i.e., substituting 1,3-pn for 1,2-pn) led to a dramatic change in the type of complex produced. While the adduct formed on adding 1,3-pn to $VO(OEt)_3$ appeared normal, the addition of HSAL at room temperature followed by a brief period of refluxing led to an orange solid that when redissolved in DMSO gave crystalline [VO(SALPN)DMSO] (**8**). It seems unlikely that steric reasons alone could account for the dramatic difference in the course of the reaction involving 1,3-pn vs 1,2-pn or en. Certainly VO(SALEN) is easily prepared from V(IV) salts and is a highly stable substance. Concomitant with the formation of the bis(Schiff base), SALPN, is reduction of the V(V) intermediate to a V(IV) species. Our present belief is that $V^{V}O_2(1,3\text{-}pnSAL)$ complex is more reductively unstable than the corresponding $V^{V}O_2(1,2\text{-}pnSAL)$ complex. In this model, a second salicylidenimine could not easily displace a terminal oxo group from V(V) but, once the metal is reduced, could easily occupy an equatorial position of the V(IV) polyhedron. Thus, a stable VO_2L is trapped with enSal while $VO_2(1,3\text{-}pnSal)$ is reduced to V(IV). The latter can subsequently undergo a second Schiff base condensation to give **8**. The question that arises next is the identity of the reductant. Clearly, salicylaldehyde is not since the reaction to form **8** is quantitative in aldehyde. The most likely candidate is the solvent (ethanol).

Although VO(SALEN) and VO(SALPN)DMSO have markedly different colors, at least some of the solution chemistry of

(27) Wiegardt, K.; Bossek, U.; Volckmar, K.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 1387.
(28) Carrano, C. J.; Nunn, C. M.; Quan, R.; Bonadies, J. A.; Pecoraro, V. L. *Inorg. Chem.* **1990**, *29*, 944.
(29) Scheidt, W. R. *Inorg. Chem.* **1973**, *12*, 1758.
(30) Root, C. A. Manuscript in preparation.

these molecules is very similar. The reactivity of VO(SALEN) with acids has been shown to be rich.[13b,c] Addition of acids with coordinating anions such as anhydrous HCl leads to displacement of the terminal oxo group to give $V^{IV}(SALEN)Cl_2$. In contrast, VO(SALEN) will disproportionate to $V^{V}O(SALEN)^+$ and $V^{III}(SALEN)$ with aqueous, nondonor acids such as $HClO_4$. Both $V^{IV}(SALEN)Cl_2$ and $V^{V}O(SALEN)^+$ are colored deep blue by strong visible charge transfer excitations. Addition of anhydrous HCl to an acetonitrile solution of VO(SALPN)DMSO or $[VO(SALPN)]_n$ leads immediately to a deep blue solution reminiscient of $V(SALEN)Cl_2$. If left open to air, this solution will slowly hydrolyze to a deep green solution which is apparently the 5-coordinate form of VO(SALPN). If water is added directly, the solution turns green and then decolorizes as the ligand is displaced under the strongly acid solution conditions. Additionally, if one adds $HClO_4$ to an acetonitrile solution of VO(SALPN)DMSO or $[VO(SALPN)]_n$, a deep blue solution is formed. We assign this specie as $VO(SALPN)^+$ by analogy to VO(SALEN) chemistry.

Solution Studies of $[VO_2(1,2\text{-pnSAL})]_2$. By analogy to $[VO_2(HSHED)]_2$, we felt it was likely that the $[VO_2(1,2\text{-pnSAL})]_2$ dimer dissociated in DMSO solution to form two monomers. Since both halves of the dimer are identical by symmetry, this possibility cannot be addressed by ^1H NMR. However, vapor pressure osmometry allowed us to answer this question in DMF at 70 °C. The molecular mass was determined to be 262 g/mol by this method compared to 260 g/mol calculated for the monomer. The ^1H NMR spectrum taken at 70 °C in DMF was unperturbed from the room temperature spectrum. Taken together, these studies confirm that the solvent breaks the weak intermolecular contacts observed in the solid state.

The monomeric $VO_2(1,2\text{-pnSAL})$ may form four pairs of enantiomers due to the chiral center on the propylenediamine backbone. The methyl substituent may be *syn* or *anti*, relative to the vanadyl oxygen, and on either the α or β carbon relative to the Schiff base imine. Two of these isomers are shown in Chart II with the respective proton assignments for α and β isomers. It should be noted that we cannot distinguish whether the methyl substituent is *syn* or *anti* with respect to the V=O. Therefore, we have shown these two isomers for illustrative purposes only.

^1H NMR (data not shown) indicates that two isomers, A and B, are present in a ratio of 85:15. As is indicated by decoupling experiments, the methyl group is α to the primary amine in the predominant isomer. A summary of the decoupling experiments described below is shown schematically in Figure 4. The amine protons are magnetically inequivalent and each has poorly resolved coupling. The resonance at 5.39 ppm is a doublet and the resonance at 4.93 ppm is a triplet. Selective irradiation of the tertiary proton of the ethyl chain (3.02 ppm) causes the collapse of the doublet at 1.15 ppm to a singlet, the two doublet of doublets at 3.97 ppm, and 3.63 ppm to two doublets (^2J = 13.5 Hz), and the amine triplet at 4.93 ppm becomes a broad singlet. The amine proton resonance at 5.39 ppm is unchanged. Irradiation at the 4.93 ppm signal causes the 5.39 ppm doublet to collapse to a singlet while irradiation of the 5.39 ppm resonance causes the 4.93 ppm triplet to collapse to a doublet (^3J = 9.5 Hz). Decoupling at 3.63 ppm collapses the doublet of doublets at 3.97 ppm to a doublet, and likewise, decoupling at 3.97 ppm collapses the doublet of doublets at 3.63 ppm to a doublet. Due to the line width of the 3.02 ppm signal ($\nu_{1/2} \sim 25$ Hz), decoupling at any frequency has little or no effect on this resonance. The amine protons were confirmed by D_2O exchange whereby the resonance at 3.02 ppm became better defined indicating the loss of ^3J coupling between the α proton and the amine protons.

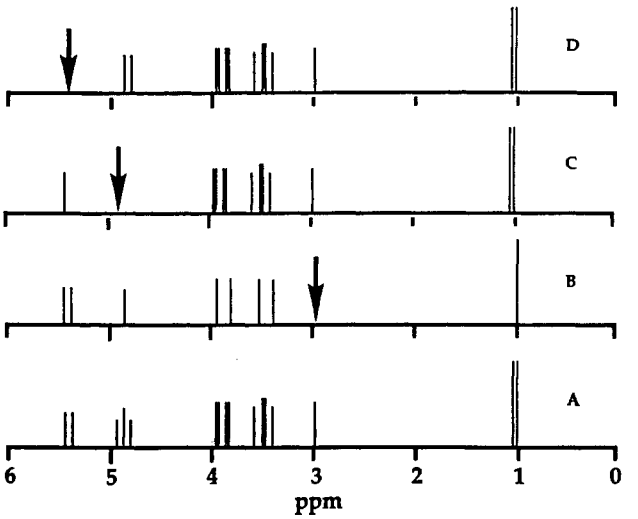


Figure 4. Schematic diagram of the results of the decoupling experiments for the solution isomer of $[VO_2(1,2\text{-pnSAL})]_2$: (A) undecoupled spectrum; (B) decoupled spectrum at 3.02 ppm indicating connectivity to the 1.15, 3.97, 3.63, and 4.93 ppm resonances; (C) decoupled spectrum at 4.93 ppm indicating connectivity to the 5.39 ppm resonance; (D) decoupled spectrum at 5.39 ppm indicating that the resonance at 4.93 ppm is coupled to one other proton (3.02 ppm).

Solution Chemistry of $VO_2(enSAL)$ with Acids, Bases, and Hydrogen Peroxide. We carried out reactions of acid, base, and hydrogen peroxide with the achiral $VO_2(enSAL)$ rather than $VO_2(1,2\text{-pnSAL})$ in order to decrease the number of isomers that would be in solution. In acetonitrile solution, addition of 1 equiv of dry HCl to $VO_2(enSAL)$ (^{51}V at −555 ppm) yields a deep blue solution which has a major resonance at −312 ppm (90%) and a minor component (10%) at −368 ppm. The latter resonance is identical to that obtained for addition of dry HCl to a vanadate solution, suggesting that a small portion of ligand has been displaced from vanadium under acidic conditions. The major species is a deep blue vanadium/enSAL complex. A similar color change can be observed for other VO_2L complexes (where L is a tridentate ligand). After addition of HCl, $VO_2(HSHED)$ will convert reversibly first to a red complex assigned as a VO(OH)(HSHED) species and then irreversibly to an unstable blue compound that may be monoxovanadium(V)–(HSHED) based on analogy to $VO(SALEN)ClO_4$.[13b,c] Another alternative is reported by Fujita and co-workers[31] who have crystallographically characterized the reddish brown monomer $VO(OCH_3)$(sal-L-ala)(CH_3OH) that can be converted to a deep blue vanadium anhydride V_2O_3(sal-L-ala)$_2$ [sal-L-ala is the Schiff base between salicylaldehyde and L-alanine]. The latter anhydride has endo and exo configurations that position the terminal oxo ligands at ≈90° from one another (as seen in $V_2O_3(SALAHE)_2$).[28] Unlike the protonation of $VO_2(HSHED)$, $VO_2(enSAL)$ bypasses the red material and goes directly to a deep blue solution, **9**, that, on the basis of the Fujita work, is most likely "$V_2O_3(enSAL)_2$". Unfortunately, the material is unstable and decomposes before solid can be recovered.

Addition of an alkyl peroxide to V_2O_3(sal-L-ala)$_2$ gives a reddish brown monomer[31] that was assigned as VO(OOR)(sal-L-ala) by analogy to [VO(dipicolinate)(*t*-BuOO)(H_2O)].[32] With this reaction in mind, we explored the chemistry of $VO_2(enSAL)$ and **9** with peroxides. Addition of hydrogen peroxide to **9** in acetonitrile yields ^{51}V resonances at −368 and −209 ppm. The signal at −368 ppm represents the sole species formed by addition of HCl to KVO_3 in acetonitrile. Addition of peroxide to this vanadate–HCl solution yields a single resonance at −209 ppm. Thus it appears that the products that result from the addition

(31) Nakajima, K.; Kojima, M.; Toriumi, K.; Saito, K.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 760.
(32) Mimoun, H.; Chaumette, P.; Mignard, M.; Saussine, L.; Fischer, J.; Weiss, R. *Nouv. J. Chim.* **1983**, *7*, 467.

of HCl and H_2O_2 to a solution of **9** do not have the ligand coordinated. Howarth and coworkers[33] have examined the ^{51}V and ^{17}O NMR spectra of aqueous vanadate peroxo complexes. The types of complexes that are formed are very sensitive to the concentration of vanadium, peroxide, and pH. While all of the chemical shifts that are reported for peroxovanadates in aqueous solution are upfield of VO_4^{3-} (−541 ppm), an assumed peroxovanadate complex resonates at −209 ppm in acetonitrile. Thus, it appears that there is a strong solvent dependence to adduct formation and the spectroscopy of these systems.

When dissolved in DMSO, VO_2(enSAL) gives a singlet at −555 ppm. In contrast to the acetonitrile studies, if perchloric acid alone is added to this solution there is only very transient (mixing time) formation of the blue species **9**. Furthermore, both the ^1H NMR and the ^{51}V NMR spectra are consistent with complex and ligand degradation. Addition of four equivalents of acid to a solution of VO_2(enSAL) results, over time, in the formation of salicylaldehyde and protonated ethylenediamine as determined by ^1H NMR.[34] Intermediates in this decomposition are also observed by ^1H NMR and probably result from protonated forms of HenSAL.

Addition of up to 10 equiv of H_2O_2 to an NMR sample of VO_2(enSAL) in DMSO caused no change in the resonance at −555 ppm nor any detectable change in the proton NMR spectrum. Addition of base ($NaOCH_3$) to a solution containing VO_2(enSAL) and H_2O_2, results only in resonances that are assigned to different oligomers of peroxovanadates without the ligand coordinated. Addition of 0.5 equiv of perchloric acid to a solution of [VO_2(enSAL)] and H_2O_2 resulted in a decrease in the resonance at −555 ppm of [VO_2(enSAL)] and the appearance of a signal at −625 ppm. Further addition of acid led to resonances at ≈−460 and −440 ppm. These latter resonances, but not the former, are also formed in the absence of ligand and are attributable to peroxovanadate complexes. The resonance at −625 ppm may result from a peroxide adduct of VO_2(enSAL). The 100 ppm upfield shift in the enSAL system is consistent with the observations of Tracey and coworkers[35] who, using ^{51}V NMR, have recently examined the aqueous formation of complexes of the type $LVO(O_2)_n$ in which L is an amino acid ligand. They also observed shifts to higher field upon peroxide coordination. However, *a priori* the ^{51}V NMR spectrum alone is not strong enough evidence to ensure this formulation is correct for a $[VO_2(enSAL)(O_2)]^{2-}$ adduct. Crans and coworkers[36] have shown that the presence of buffers can have a significant effect on equilibrium concentrations of the various vanadate oligomers. Thus, a peroxovanadate complex that is stabilized in the presence of ligand, but without ligand coordination (e.g., through hydrogen bonding), could generate the −665 ppm signal. These data demonstrate that VO_2(enSAL) does not react with hydrogen peroxide in neutral DMSO solution and decomposes significantly in acidic solution with hydrogen peroxide present.

These observations clearly illustrate that even apparently robust high valent vanadium coordination compounds are remarkably susceptible to complex decomposition in the presence of acids and bases, conditions which often favor the formation of vanadium peroxide ligand adducts.[32] The known peroxovanadium complexes with coordinated tridentate ligands often are dianions and incorporate at least one weakly basic carboxylate functional group. One reason for success with this ligand type may be that the acidic conditions needed to form peroxide complexes with vanadium leads to protonation of stronger bases such as amines and the loss of these ligands from the metal coordination sphere. Subsequently, the equilibrium between vanadate plus free ligand to give protonated $VO_2(HenSAL)^+$ can be driven toward reactants when, in the presence of H_2O_2, highly stable peroxovanadates are formed. Carboxylates (or possibly imidazoles) with lower pK_a values would be expected to be more resisitant to this decomposition pathway and, therefore, may be more likely to yield functional models for vanadium haloperoxidase.

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Supplementary Material Available: Table S7, giving a complete crystallographic summary for **5A** and **8**, tables of anisotropic thermal parameters, hydrogen atom fractional coordinates, bond lengths, and bond angles for **5A** and **8** (Tables S'9–S12 and S14–S17, respectively), and text giving synthetic procedures for the preparation of **1–4**, **6**, and **7** with complete analytical data (14 pages). Ordering information is given on any current masthead page.

(33) (a) Harrison, A. T.; Howarth, O. W. *J. Chem. Soc., Dalton Trans*, **1985**, 1173. (b) Heath, E.; Howarth, O. W. *J. Chem. Soc., Dalton Trans*, **1981**, 1105. (c) Howarth, O. W.; Hunt, J. R. *J. Chem. Soc., Dalton Trans*. **1979**, 1388.

(34) The identity of the decomposition products was confirmed by collecting the spectrum of salicylaldehyde, H_2SALEN, and ethylenediamine under identical conditions.

(35) Tracey, A. S.; Jaswal, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 3835.

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